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Dielectric and mechanical behaviour of polyurethane networks from poly(oxypropylene)diols or -triols and diisocyanate

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Summary

Thermally stimulated depolarization currents and dielectric and dynamic mechanical behaviour of polyurethane networks prepared from poly(oxypropylene)-diols or -triols and 4,4'-diphenylmethane diisocyanate were studied. While the frequency and temperature positions of mechanical and dielectric functions are predominantly determined by the concentration of polar urethane groups in the network chain, the equilibrium modulus correlates with network chain length. The effect of the chain polarity on the shape of loss permittivity vs. frequency curves is more pronounced in the low frequency region than in the high frequency one and is practically the same for stoichiometric and off-stoichiometric networks measured earlier.

Introduction

Covalently crosslinked polyurethane systems are of great practical and theoretical importance and the relations between their structure and physical properties have been widely studied.[1,2] Networks based on poly(oxypropylene)triols and diisocyanate are homogeneous and serve as model systems for testing relations between the structure, mechanical and dielectric behaviour[3-5]. Due to a comparatively simple build-up of the network structure from hydroxy and isocyanate groups, full description of structure could be made[2-4]. By changing the initial ratio of the components ($r_H = [OH]/[NCO]$), networks with a broad variation in structure (the crosslinking density and the network topology[5,6]) were obtained. It was found[5,6] that the frequency and temperature position of dielectric and mechanical functions in the main transition region is affected predominantly by the concentration of polar urethane groups. On the other hand, the shape of mechanical functions in the main transition region was affected also by the detailed topology of network chains, determined by the r_H value. The crosslinking density can be changed also by varying the length of polyols or polyisocyanates at stoichiometric ratio of reactive groups, but the structure obtained in this way is different from that obtained by changing the ratio of the reactive groups, r_H. While the stoichiometric networks have a simple structure of elastically active network chains (EANC's), the structure of EANC's in off-stoichiometric networks is complex, with various dangling chains attached to the backbone chain[6].

In this contribution thermally stimulated depolarization currents together with the dielectric and mechanical behaviour of polyurethane networks are studied. The networks were prepared from poly(oxypropylene)diols or -triols and diisocyanate at stoichiometric initial molar ratio of hydroxy and isocyanate groups. The crosslinking density and the polarity (number of urethane groups in the chains) are controlled by the length and/or the number of diols in the EANC. The viscoelastic behaviour of these networks is compared with the behaviour of similar off-stoichiometric networks measured earlier[5].

Experimental

Sample preparation: Two poly(oxypropylene)triols (PPT, LHT-240 with number-average molecular weight $M_n = 710$ and LG-56 with $M_n = 2630$) and two poly(oxypropylene)diols (PPD, $M_n = 400$ and $M_n = 1000$) were dried by azeotropic distillation with benzene. The concentration of hydroxy groups, c_{OH}, was determined by potentiometric titration (c_{OH} =6.94, 1.8, 8.7 and 3.01 wt.% for LHT-240, LG-56, PPD(400) and PPD(1000), respectively) and the water content by coulometry (in all cases water content was less than 0.002 wt.%). 4,4'-diphenylmethane diisocyanate (MDI) was distilled under vacuum and then recrystallized twice from dry hexane (concentration of NCO groups, $c_{NCO} = 33.6$ wt.%). All the components were mixed together, the mixture was stirred for ~15 min in dry nitrogen at 60°C. After that, dibutyltin dilaurate catalyst (~0.01 wt. %) was added and the mixture was homogenized. The polymerization proceeded in Teflon molds at 80°C for 24h (full conversion of reactive groups). Five networks S1 - S5 were prepared with a stoichiometric initial ratio of hydroxy to isocyanate groups $r_H = ([OH]_{PPD} + [OH]_{PPT})/[NCO]_{MDI} = 1$ and with various lengths of EANC in the range from $M_n = 1970$ to 4500. Corresponding amounts of diols, triols and MDI in the mixturre were determined from the structure of networks S1 - S5:

S1: (1/3)LHT-MDI-PPD(1000)-MDI-(1/3)LHT, $M_n = 1970$
S2: (1/3)LG-MDI-PPD(1000)-MDI-(1/3)LG, $M_n = 3260$
S3: (1/3)LG-MDI-PPD(1000)-MDI-PPD(1000)-MDI-(1/3)LG, $M_n = 4500$
S4: (1/3)LHT-MDI-PPD(1000)-MDI-PPD(1000)-MDI-PPD(1000)-MDI-(1/3)LHT, $M_n = 4480$
S5:(1/3)LHT-MDI-PPD(400)-MDI-PPD(1000)-MDI-PPD(400)-MDI-(1/3)LHT, $M_n = 3300$

Networks S2 and S5 and S3 and S4 differ in polarity (amount of MDI).

Measurements of permittivity and thermally stimulated depolarization currents (TSDC): The dependencies of the complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ (ε' is the storage and ε'' is the loss component) on frequency *f* and temperature *T* were measured by a Hewlett-Packard 4192A LF Impedance Analyzer in the frequency range from 10Hz to 10MHz. For TSDC measurements the samples were heated 50K above glass transition temperatures; then electric field of intensity 1MV/m was applied for 10 min and the samples were quenched down to liquid nitrogen temperature. TSDC was recorded using a Keithley 610C Electrometer at a heating rate 3K/min. For both types of measurement the same measuring condenser with sandwich-like sample arrangement was used. From TSDC measurements the temperature T_m^1, corresponding to the peak temperature of the depolaarization current in the main transition region, was determined.

For all neetworks the dielectric data in the main transition reegion could be described with a reasonable accuracy as a superposition of two terms

$$\varepsilon^* = \varepsilon_d^* + \varepsilon_c^* \,. \qquad (1)$$

The first term (dielectric contribution) is given by the Havriliak-Negami formula[7] in the form

$$\varepsilon_d^* = B \cdot (1 + (jf/f_r)^{\alpha})^{-\beta} \qquad (2)$$

where B, α, β and f_r are temperature-dependent parameters. The parameter f_r is related to the frequency f_m, at which the loss component of permittivity attains its maximum value, by the formula $(f_m/f_r)^{\alpha} = \sin\gamma / \sin(\beta\gamma)$, where $\gamma = (\alpha\pi/2)/(\beta + 1)$. To describe the temperature dependence of the frequency f_m, the Williams-Landel-Ferry (WLF) equation[8] is used

$$\log f_m = \log f_s + 8.86(T - T_s)/(101.6 + T - T_s) \qquad (3)$$

where T_s is the charasteristic temperaature and f_s is constant.

The second contribution is due to the DC conductivity and becomes dominant at low frequencies and high temperatures. We use the expression[9]

$$\varepsilon_c^* = (jf_c/f)^c \cdot \exp(-A/(T - T_c)) \qquad (4)$$

where T_c, f_c and A are constants. It should be noticed that the standard Arrhenius temperature dependence for the conductivity turned out to be inappropriate and therefore a more general relation of the Vogel-Fulcher-Tamman (VFT) type[9] had to be used. It was also found that the value of exponent slightly differs from unity, suggesting that conductivity has, at least partially, some relaxational character. Computer program was developed for fitting eq.(1) to the experimental data. The program was based on the Marquardt fitting procedure[10].

Dynamic mechanical measurements: The complex shear modulus $G^* = G' + jG''$ (G' is the storage and G'' is the loss modulus component) was measured with a Rheometrics SYS-4 apparatus at frequency $f = 1\text{Hz}$ in the temperature range from 200 to 300K. The heating rate was 2K/min. From the temperaature dependence of the loss modulus G'' the temperaature T_m^2, corresponding to the peak temperature in the main transition region, was determined.

Results and Discussion

Frequency and temperature dependences: As an example, both components of complex permittivity are plotted in dependence on frequency *f* for network S1 in

Fig.1. The temperature range corresponds mainly to the main transition region and to lesser extent also to the secondary relaxation region at low temperatures. An asymmetrical shape of the loss component ε'' vs. frequency curves in the main transition region was found for all networks; in all cases the low frequency side is steeper than the high frequency one. The experimental dependencies of ε'' on f at higher temperatures (corresponding to the main transition) were found to satisfy eqs (1)-(4) and the distribution parameters α and β were determined. As a slight dependence of $\alpha$and β on temperature was found (the change did not exceed 10% for both parameters), the frequency-temperature superposition could not be applied to the dielectric data in the main transition region. The secondary (low temperature) process was very broad and its intensity was about two order of magnitude lower than that of the main transition process. For this reason only frequency position of the ε'' maximum, f^s_m, was determined and no fitting procedure was applied to this process.

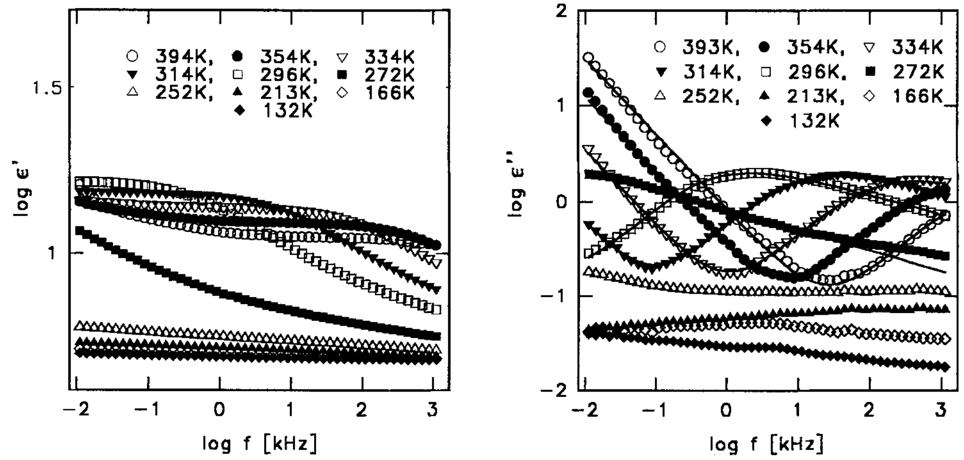

Fig.1. Frequency dependence of the storage $\varepsilon'$and of the loss ε''components of complex permittivity for sample 1. Hawriliak-Negami fit for loss component ε'' is shown by full lines

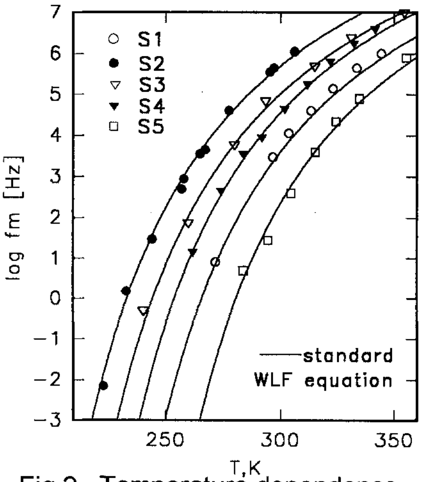

Fig.2. Temperature dependence of the frequencies of the maxima f_m

From the frequency dependencies of the loss permittivity ε'' in the main transition region the frequencies of the maxima, f_m, were determined. For all networks temperature dependencies of f_m satisfy the WLF equation (3) and characteristic temperatures T_s could be determined.

In Fig.2 the dependencies of f_m on$T$ are plotted together with theoretical WLF curves (eq.(3)), shown as full lines.

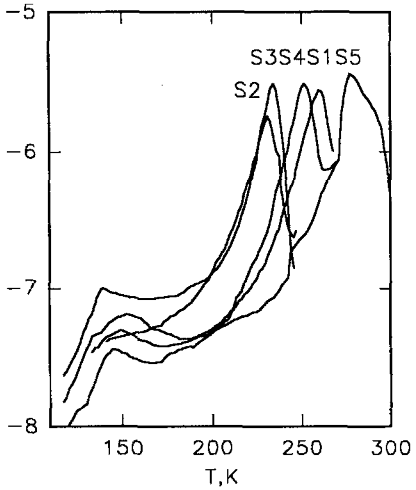

Fig.3. Temperature dependence of TSDC curves

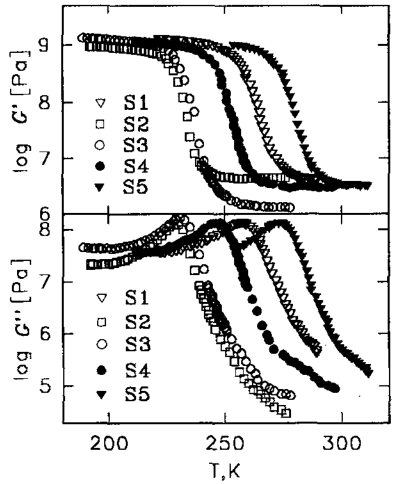

Fig.4. Temperature dependencies of the storage G' and loss G'' moduli

Fig.3 shows TSDC curves of all networks. The depolarization current maxima, T_m^1, located between 200 K and 275 K correspond to the main transition region. At temperature T~140K a secondary transition can be seen. A similar low-temperature transition in the glassy region was also found in dielectric behaviour (Fig.1). The temperature dependence of the frequencies of the maxima f_m^β of the secondary dielectric transition corresponds to the Arrhenius equation with the activation energy U ~ 0,4 eV for all networks.

The temperature dependencies of the storage G' and loss G'' moduli can be seen in Fig.4; the shape of these dependencies is practically unaffected by the network composition. From the temperature dependencies of the loss moduli G'' the temperatures of the maxima, T_m^2, were determined. While storage modulus G' in the glassy region is about the same for all networks, its value in the rubbery region depends on M_n of network chain. From the values G'_e measured at temperatures $T_m^2 + 50\,\mathrm{K}$ (rubbery state for all samples) the concentrations of elastically active network chains, ν_e, and the molecular weight between junctions, M_c, were determined from the relation

$$\nu_e = G'_e/R(T_m^2 + 50) = \rho/M_c \qquad (5)$$

where R is the gas constant, ρ is the density and M_c molecular weight of EANC. The calculated M_c values for networks S1 - S5 (M_c=2021,3140,4450, 4280,3120) correlate with M_n.

Effect of the network polarity on the shape and temperature position: To characterize the polarity of our stoichiometric networks S1 - S5 we introduced parameter $p = 2n/M_n$, where n is number of MDI molecules incorporated into network chain. The value of $1/p$ is then the molecular weight of the polyoxypropylene chain which corresponds to one NCO (or urethane) group. For off-stoichiometric

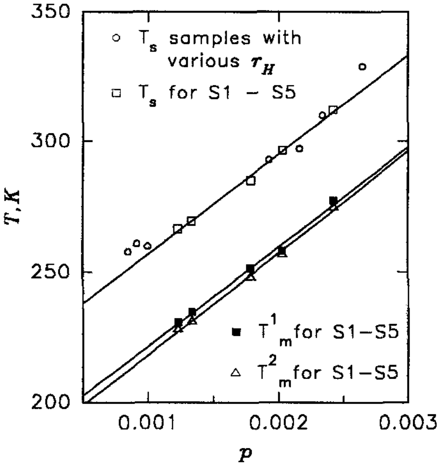

Fig.5. Dependence of T_s, T^1_m and T^2_m temperatures on polarity p

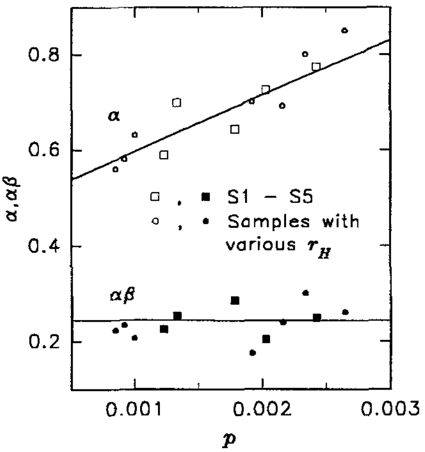

Fig.6. Dependence of Hawriliak-Negami shape parameters α and αβ on polarity p

networks[3-5] prepared from short (LTH-240) or long (LG-56) triol and MDI at various initial ratios of hydroxy to isocyanate groups $r_H = [OH]/[NCO] = 1.0$ to 1.7 a similar parameter $p = 1/(r_H \cdot M_n^{PPT}/3 + 125)$ can be calculated. In futher discussion we include the dielectric parameters obtained on S1 - S5 networks as well as those obtained previously[3-5] on off-stoichiometric networks.

From Fig.5 it is obvious that temperatures T_s, T^1_m and T^2_m (characterizing the temperature position of the main transition) increase with increasing polarity p with the same slope. While T^1_m and T^2_m determined from TSDC and from G'' curves are roughly the same, the T_s temperatures from dielectric measurements are about 35 K higher than T^1_m or T^2_m (T^1_m and T^2_m are closer to the glass transition temperature T_g). It is important to notice that T_s temperatures of stoichiometric networks S1-S5 and off-stoichiometric networks measured earlier[5] lie on the same T_s vs. p dependence. This means that the temperature (and also frequency) position of the main transition region of networks is mainly determined by the polarity (amount of MDI) of the system and the length of EANC's has minor effect.

The main process distribution parameter α (characterizing the low-frequency slope of $\log \varepsilon''$ vs. $\log f$ plot) and the product αβ (characterizing the high- frequency slope) in dependence on polarity p are shown in Fig.6 for temperature 300 K. Within experimental scatter the distribution parameters of stoichiometric S1 - S5 and off- stoichiometric networks measured earlier[5] lie on the same α vs. p or αβ vs. p dependencies. This means that the shape of the main dielectric process (similarly as temperaature position of the transition) is predominantly affected by the polarity of the system. While the product αβ is almost independent of p, the value of α increases with p. This means that the effect of polarity on the shape of permittivity curves is higher in the low-frequency region than in the high frequency one. The broadering of the low-frequency region (lowering the α values) with decreasing p means that the participation of longer relaxation times in dielectric spectrum increases. As with increasing p the molecular weight of the polyoxypropylene chain (which corresponds to one urethane group) increases, the broadering of the low-frequency region is probably caused by the increasing length of polyoxypropylene chain betwen urethane groups.

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